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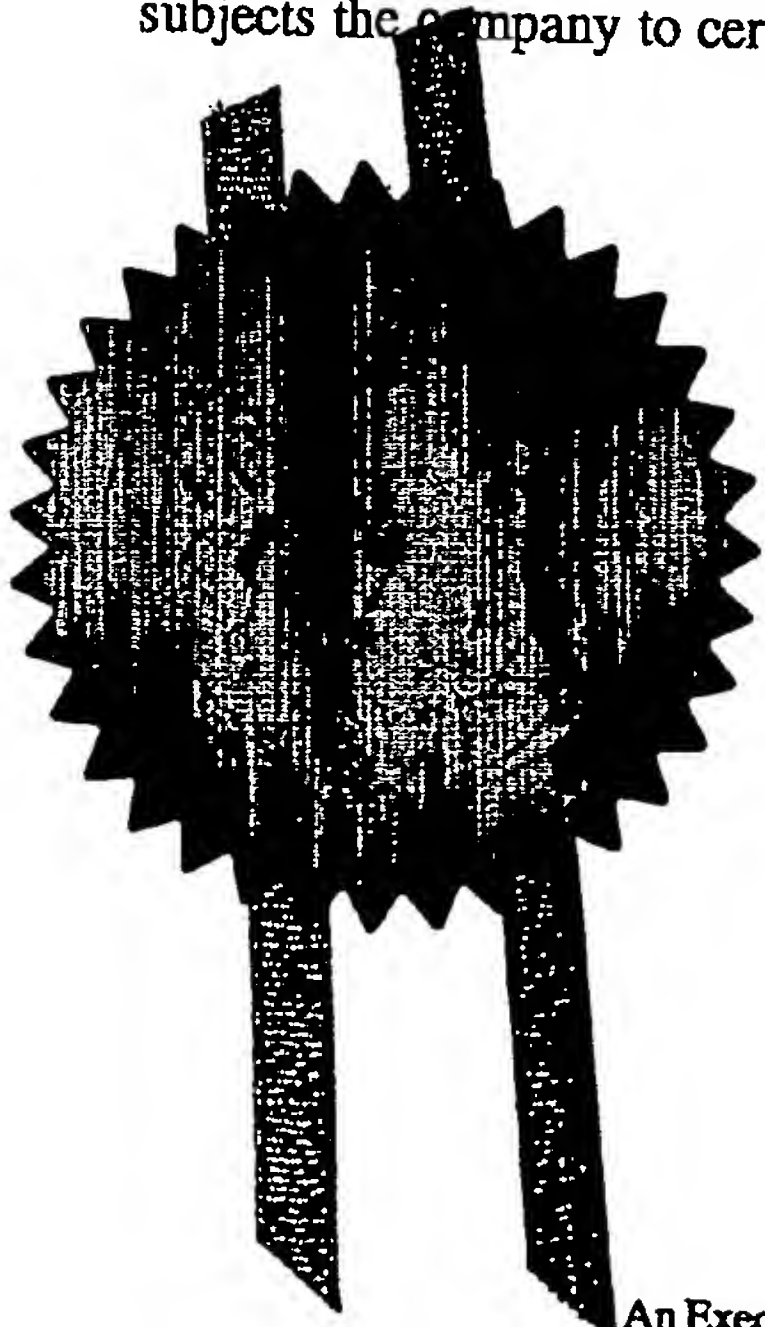
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Request for grant of a patent

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1. Your Reference

DXM/CAL/Y693

2. Application number

0315536.3

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4. Title of the invention

PROCESS FOR THE HYDROFORMYLATION OF
ETHYLENICALLY UNSATURATED
COMPOUNDS

5. Name of agent

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Patents ADP number

190001 ✓

6. Priority claimed to:

Country

Application number

Date of filing

7. Divisional status claimed from:

Number of parent application

Date of filing

8. Is a statement of inventorship and
of right to grant a patent required in
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YES

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Description

31 (x 2)

Claim(s)

10 (x 2) *12*

Abstract

2 (x 2)

Drawing(s)

0

10. If you are also filing any of the following, state how many against each item

Priority documents

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Statement of inventorship and right to grant a patent (PF 7/77)

Request for a preliminary examination and search (PF 9/77)

Request for substantive examination (PF 10/77)

Any other documents (please specify)

11.

We request the grant of a patent on the basis of this application.
Signature *Appleyard Lees* Date

APPLEYARD LEES

03 July 2003

12. Contact

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DUPLICATE

1

PROCESS FOR THE HYDROFORMYLATION OF ETHYLENICALLY
UNSATURATED COMPOUNDS

The present invention relates to the hydroformylation of
5 ethylenically unsaturated compounds by reaction with
carbon monoxide and hydrogen in the presence of a catalyst
system.

The hydroformylation of ethylenically unsaturated
10 compounds using carbon monoxide in the presence of
hydrogen and a catalyst comprising a group VIII metal,
example, rhodium, and a phosphine ligand, example an alkyl
phosphine, cycloalkyl phosphine, aryl phosphine, pyridyl
phosphine or bidentate phosphine, has been described in
15 numerous patents and patent applications.

WO 96/19434 disclosed that a particular group of bidentate
phosphine compounds can provide stable catalysts in
carbonylation reaction systems, and the use of such
20 catalysts leads to reaction rates which were significantly
higher than those previously disclosed.

WO 01/68583 discloses carbonylation processes for higher
alkenes of three or more carbon atoms.

25

WO 02/76996, for example, discloses a method for producing
diphosphines, and their use as co-catalyst for
hydroformylating olefins. WO 02/20448 similarly discloses
the preparation of arylphosphines for the rhodium-
30 catalysed hydroformylation of alkenes.

Although catalyst systems have been developed which
exhibit reasonable stability during the hydroformylation

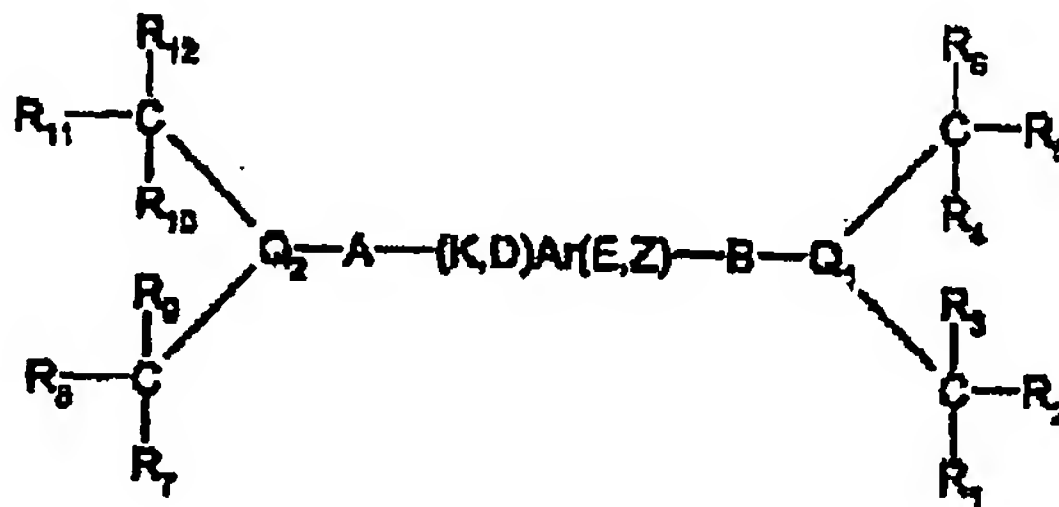
process and permit relatively high reaction rates and regioselectivity between linear and branched aldehyde products, there still exists a need for improved catalyst systems. Suitably, the present invention aims to provide
 5 an improved catalyst for hydroformylating ethylenically unsaturated compounds.

Surprisingly, it has been found that improved selectivity of the linear aldehyde product compared to the branched
 10 aldehyde product can be obtained than by using catalyst systems of the prior art.

According to the first aspect of the present invention there is provided a process for the hydroformylation of
 15 ethylenically unsaturated compounds, which process comprises reacting said ethylenically unsaturated compound with carbon monoxide and hydrogen, in the presence of a catalyst system and a solvent, the catalyst system obtainable by combining:

20

- a) a metal of Group VIII or a compound thereof; and
- b) a bidentate phosphine of general formula (I)



25 wherein:

Ar is a bridging group comprising an optionally substituted aryl moiety to which the phosphorus atoms are linked on available adjacent carbon atoms;

5 A and B each independently represent lower alkylene;

K, D, E and Z are substituents of the aryl moiety (Ar) and each independently represent hydrogen, lower alkyl, aryl, Het, halo, cyano, nitro, OR^{19} , $OC(O)R^{20}$, $C(O)R^{21}$, $C(O)OR^{22}$,
10 $NR^{23}R^{24}$, $C(O)NR^{25}R^{26}$, $C(S)R^{25}R^{26}$, SR^{27} , $C(O)SR^{27}$, or $-J-Q^3(CR^{13}(R^{14})(R^{15}))CR^{16}(R^{17})(R^{18})$ where J represents lower alkylene; or two adjacent groups selected from K, Z, D and E together with the carbon atoms of the aryl ring to which they are attached form a further phenyl ring, which is
15 optionally substituted by one or more substituents selected from hydrogen, lower alkyl, halo, cyano, nitro, OR^{19} , $OC(O)R^{20}$, $C(O)R^{21}$, $C(O)OR^{22}$, $NR^{23}R^{24}$, $C(O)NR^{25}R^{26}$, $C(S)R^{25}R^{26}$, SR^{27} or $C(O)SR^{27}$;

20 R^1 to R^{18} each independently represent lower alkyl, aryl, or Het;

R^{19} to R^{27} each independently represent hydrogen, lower alkyl, aryl or Het;

25

Q^1 , Q^2 and Q^3 (when present) each independently represent phosphorous, arsenic or antimony and in the latter two cases references to phosphine or phosphorous above are amended accordingly,

30

the process characterised in that a chlorine moiety is present in at least one of the said Group VIII metal compound or said solvent.

Such a process is referred to hereinafter as "the process of the invention".

- 5 Preferably, when K, D, E or Z represent -J-
Q³(CR¹³(R¹⁴)(R¹⁵))CR¹⁶(R¹⁷)(R¹⁸), the respective K, D, E or Z
is on the aryl carbon adjacent the aryl carbon to which A
or B is connected or, if not so adjacent, is adjacent a
remaining K, D, E or Z group which itself represents -J-
10 Q¹(CR¹³(R¹⁴)(R¹⁵))CR¹⁶(R¹⁷)(R¹⁸).

Suitably, the process of the invention may be used to
catalyse the hydroformylation of an ethylenically
unsaturated compound in the presence of carbon monoxide
15 and hydrogen, i.e. the process of the invention may
catalyse the conversion of an ethylenically unsaturated
compound to the corresponding aldehyde. Conveniently, the
process of the invention will show an increased
selectivity to the linear aldehyde product, compared to
20 the branched aldehyde product, in comparison with similar
processes but where the chlorine moiety is not present.
Conveniently, the process of the invention may utilise
highly stable compounds under typical hydroformylation
reaction conditions such that they require little or no
25 replenishment. Conveniently, the process of the invention
may have an increased rate of the hydroformylation
reaction of an ethylenically unsaturated compound compared
to known processes. Conveniently, the process of the
invention may promote high conversion rates of the
30 ethylenically unsaturated compound, thereby yielding the
desired product in high yield with little or no
impurities. Consequently, the commercial viability of the
hydroformylation process, such as the hydroformylation of

an ethylenically unsaturated compound, may be increased by employing the process of the invention.

The term "Ar" or "aryl" when used herein, includes six-to-
5 ten-membered carbocyclic aromatic groups, such as phenyl
and naphthyl, which groups are optionally substituted
with, in addition to K, D, E or Z, one or more
substituents selected from aryl, lower alkyl (which alkyl
group may itself be optionally substituted or terminated
10 as defined below), Het, halo, cyano, nitro, OR^{19} , $OC(O)R^{20}$,
 $C(O)R^{21}$, $C(O)OR^{22}$, $NR^{23}R^{24}$, $C(O)NR^{25}R^{26}$, SR^{27} , $C(O)SR^{27}$ or
 $C(S)NR^{25}R^{26}$ wherein R^{19} to R^{27} each independently represent
hydrogen, aryl or lower alkyl (which alkyl group may
itself be optionally substituted or terminated as defined
15 below).

The term "Het", when used herein, includes four-to-twelve-
membered, preferably four-to-ten-membered ring systems,
which rings contain one or more heteroatoms selected from
20 nitrogen, oxygen, sulfur and mixtures thereof, and which
rings may contain one or more double bonds or be non-
aromatic, partly aromatic or wholly aromatic in character.
The ring systems may be monocyclic, bicyclic or fused.
Each "Het" group identified herein is optionally
25 substituted by one or more substituents selected from
halo, cyano, nitro, oxo, lower alkyl (which alkyl group
may itself be optionally substituted or terminated as
defined below) OR^{19} , $OC(O)R^{20}$, $C(O)R^{21}$, $C(O)OR^{22}$, $NR^{23}R^{24}$,
 $C(O)NR^{25}R^{26}$, SR^{27} , $C(O)SR^{27}$ or $C(S)NR^{25}R^{26}$ wherein R^{19} to R^{27}
30 each independently represent hydrogen, aryl or lower alkyl
(which alkyl group itself may be optionally substituted or
terminated as defined below). The term "Het" thus includes
groups such as optionally substituted azetidiny,

pyrrolidinyl, imidazolyl, indolyl, furanyl, oxazolyl,
isoxazolyl, oxadiazolyl, thiazolyl, thiadiazolyl,
triazolyl, oxatriazolyl, thiatriazolyl, pyridazinyl,
morpholinyl, pyrimidinyl, pyrazinyl, quinolinyl,
5 isoquinolinyl, piperidinyl, pyrazolyl and piperazinyl.
Substitution at Het may be at a carbon atom of the Het
ring or, where appropriate, at one or more of the
heteroatoms.

10 "Het" groups may also be in the form of an N oxide.

The term "lower alkyl" when used herein, means C₁ to C₁₀
alkyl and includes methyl, ethyl, propyl, butyl, pentyl,
hexyl and heptyl groups. Unless otherwise specified, alkyl
15 groups may, when there is a sufficient number of carbon
atoms, be linear or branched, be saturated or unsaturated,
be cyclic, acyclic or part cyclic/acyclic, and/or be
substituted or terminated by one or more substituents
selected from halo, cyano, nitro, OR¹⁹, OC(O)R²⁰, C(O)R²¹,
20 C(O)OR²², NR²³R²⁴, C(O)NR²⁵R²⁶, SR²⁷, C(O)SR²⁷, C(S)NR²⁵R²⁶,
aryl or Het, wherein R¹⁹ to R²⁷ each independently
represent hydrogen, aryl or lower alkyl, and/or be
interrupted by one or more oxygen or sulfur atoms, or by
silano or dialkylsilcon groups.

25

Lower alkyl groups which R¹, R², R³, R⁴, R⁵, R⁶, R⁷, R⁸, R⁹,
R¹⁰, R¹¹, R¹², R¹³, R¹⁴, R¹⁵, R¹⁶, R¹⁷, R¹⁸, R¹⁹, R²⁰, R²¹, R²²,
R²³, R²⁴, R²⁵, R²⁶, R²⁷, K, D, E and Z may represent and with
which aryl and Het may be substituted, may, when there is
30 a sufficient number of carbon atoms, be linear or
branched, be saturated or unsaturated, be cyclic, acyclic
or part cyclic/acyclic, and/or be interrupted by one or
more of oxygen or sulfur atoms, or by silano or

dialkylsilicon groups, and/or be substituted by one or more substituents selected from halo, cyano, nitro, OR^{19} , $OC(O)R^{20}$, $C(O)R^{21}$, $C(O)OR^{22}$, $NR^{23}R^{24}$, $C(O)NR^{25}R^{26}$, SR^{27} , $C(O)SR^{27}$, $C(S)NR^{25}R^{26}$, aryl or Het wherein R^{19} to R^{27} each
5 independently represent hydrogen, aryl or lower alkyl.

Similarly, the term "lower alkylene" which A, B and J (when present) represent in a compound of formula (I), when used herein, includes C_1 to C_{10} groups which can be
10 bonded at two places on the group and is otherwise defined in the same way as "lower alkyl".

Halo groups with which the above-mentioned groups may be substituted or terminated include fluoro, chloro, bromo
15 and iodo groups.

Where a compound of the formula (I) contains an alkenyl group, cis (E) and trans (Z) isomerism may also occur. The present invention includes the individual stereoisomers of
20 the compounds of formula (I) and, where appropriate, the individual tautomeric forms thereof, together with mixtures thereof. Separation of diastereoisomers or cis and trans isomers may be achieved by conventional techniques, e.g. by fractional crystallisation,
25 chromatography or H.P.L.C. of a stereoisomeric mixture of a compound of the formula (I) or a suitable salt or derivative thereof. An individual enantiomer of a compound of the formula (I) may also be prepared from a corresponding optically pure intermediate or by
30 resolution, such as by H.P.L.C. of the corresponding racemate using a suitable chiral support or by fractional crystallisation of the diastereoisomeric salts formed by

reaction of the corresponding racemate with a suitable optically active acid or base, as appropriate.

All stereoisomers are included within the scope of the
5 process of the invention.

It will be appreciated by those skilled in the art that the compounds of formula (I), i.e. (b) above, may function as ligands that coordinate with the Group VIII metal or
10 compound thereof, i.e. (a) above, to form the compounds for use in the invention. Typically, the Group VIII metal or compound thereof, i.e. (a) above, coordinates to the one or more phosphorous, arsenic and/or antimony atoms of the compound of formula (I).

15

Preferably, R^1 to R^{18} each independently represent lower alkyl or aryl. More preferably, R^1 to R^{18} each independently represent C_1 to C_6 alkyl, C_1 - C_6 alkyl phenyl (wherein the phenyl group is optionally substituted as
20 defined herein) or phenyl (wherein the phenyl group is optionally substituted as defined herein). Even more preferably, R^1 to R^{18} each independently represent C_1 to C_6 alkyl, which is optionally substituted as defined herein. Most preferably, R^1 to R^{18} each represent non-substituted
25 C_1 to C_6 alkyl such as methyl, ethyl, n-propyl, iso-propyl, n-butyl, iso-butyl, tert-butyl, pentyl, hexyl and cyclohexyl.

Alternatively, or additionally, each of the groups R^1 to
30 R^3 , R^4 to R^6 , R^7 to R^9 , R^{10} to R^{12} , R^{13} to R^{15} or R^{16} to R^{18} together independently may form cyclic structures such as 1-norbornyl or 1-norbornadienyl. Alternatively, one or

more of the groups may represent a solid phase to which the ligand is attached.

In a particularly preferred embodiment of the present invention R^1 , R^4 , R^7 , R^{10} , R^{13} and R^{16} each represent the same lower alkyl, aryl or Het moiety as defined herein, R^2 , R^5 , R^8 , R^{11} , R^{14} and R^{17} each represent the same lower alkyl, aryl or Het moiety as defined herein, and R^3 , R^6 , R^9 , R^{12} , R^{15} and R^{18} each independently represent the same lower alkyl, aryl or Het moiety as defined herein. More preferably R^1 , R^4 , R^7 , R^{10} , R^{13} and R^{16} each independently represent the same C_1 - C_6 alkyl, particularly non-substituted C_1 - C_6 alkyl, such as methyl, ethyl, n-propyl, iso-propyl, n-butyl, iso-butyl, tert-butyl, pentyl, hexyl or cyclohexyl; R^2 , R^5 , R^8 , R^{11} , R^{14} and R^{17} each independently represent the same C_1 - C_6 alkyl as defined above; and R^3 , R^6 , R^9 , R^{12} , R^{15} and R^{18} each independently represent the same C_1 - C_6 alkyl as defined above. For example: R^1 , R^4 , R^7 , R^{10} , R^{13} and R^{16} each represent methyl; R^2 , R^5 , R^8 , R^{11} , R^{14} and R^{17} each represent ethyl; and, R^3 , R^6 , R^9 , R^{12} , R^{15} and R^{18} each represent n-butyl or n-pentyl.

In an especially preferred embodiment of the present invention each R^1 to R^{18} group represents the same lower alkyl, aryl, or Het moiety as defined herein. Preferably, each R^1 to R^{18} represents the same C_1 to C_6 alkyl group, particularly non-substituted C_1 - C_6 alkyl, such as methyl, ethyl, n-propyl, iso-propyl, n-butyl, iso-butyl, tert-butyl, pentyl, hexyl and cyclohexyl. Most preferably, each R^1 to R^{18} represents methyl.

In the compound of formula (I), preferably each Q^1 , Q^2 and Q^3 (when present) is the same. Most preferably, each Q^1 , Q^2 and Q^3 (when present) represents phosphorous.

5 Preferably, in the compound of formula (I), A, B and J (when present) each independently represent C_1 to C_6 alkylene which is optionally substituted as defined herein, for example with lower alkyl groups. Preferably, the lower alkylene groups which A, B and J (when present)
10 represent are non-substituted. A particular preferred lower alkylene which A, B and J may independently represent is $-CH_2-$ or $-C_2H_4-$. Most preferably, each of A, B and J (when present) represent the same lower alkylene as defined herein, particularly $-CH_2-$.

15

Preferably, in the compound of formula (I) when K, D, E or Z does not represent $-J-Q^3(CR^{13}(R^{14})(R^{15}))CR^{16}(R^{17})(R^{18})$, K, D, E or Z represents hydrogen, lower alkyl, phenyl or lower alkylphenyl. More preferably, K, D, E or Z represent
20 hydrogen, phenyl, C_1 - C_6 alkylphenyl or C_1 - C_6 alkyl, such as methyl, ethyl, propyl, butyl, pentyl and hexyl. Most preferably, K, D, E or Z represents hydrogen.

Preferably, in the compound of formula (I) when K, D, E
25 and Z together with the carbon atoms of the aryl ring to which they are attached do not form a phenyl ring, K, D, E and Z each independently represent hydrogen, lower alkyl, phenyl or lower alkylphenyl. More preferably, K, D, E and Z each independently represent hydrogen, phenyl, C_1 - C_6
30 alkylphenyl or C_1 - C_6 alkyl, such as methyl, ethyl, propyl, butyl, pentyl and hexyl. Even more preferably, K, D, E and Z represent the same substituent. Most preferably, they represent hydrogen.

11

Preferably, in the compound of formula (I) when K, D, E or Z does not represent $-J-Q^3(CR^{13}(R^{14})(R^{15}))CR^{16}(R^{17})(R^{18})$ and K, D, E and Z together with the carbon atoms of the aryl ring to which they are attached do not form a phenyl ring, each of K, D, E and Z represent the same group selected from hydrogen, lower alkyl, aryl, or Het as defined herein; particularly hydrogen or C_1-C_6 alkyl (more particularly unsubstituted C_1-C_6 alkyl), especially hydrogen.

Preferably, in the compound of formula (I) when two of K, D, E and Z together with the carbon atoms of the aryl ring to which they are attached form a phenyl ring, then the phenyl ring is optionally substituted with one or more substituents selected from aryl, lower alkyl (which alkyl group may itself be optionally substituted or terminated as defined below), Het, halo, cyano, nitro, OR^{19} , $OC(O)R^{20}$, $C(O)R^{21}$, $C(O)OR^{22}$, $NR^{23}R^{24}$, $C(O)NR^{25}R^{26}$, SR^{27} , $C(O)SR^{27}$ or $C(S)NR^{25}R^{26}$ wherein R^{19} to R^{27} each independently represent hydrogen or lower alkyl (which alkyl group may itself be optionally substituted or terminated as defined herein). More preferably, the phenyl ring is not substituted by any substituents i.e. it bears hydrogen atoms only.

25

Preferred compounds of formula (I) include those wherein:

A and B each independently represent unsubstituted C_1 to C_6 alkylene;

30

K, D, Z and E each independently represent hydrogen, C_1-C_6 alkyl, phenyl, C_1-C_6 alkylphenyl or $-J-Q^3(CR^{13}(R^{14})(R^{15}))CR^{16}(R^{17})(R^{18})$ where J represents

unsubstituted C_1 to C_6 alkylene; or two of K, D, Z and E together with the carbon atoms of the aryl ring to which they are attached form a phenyl ring which is optionally substituted by one or more substituents selected from
5 lower alkyl, phenyl or lower alkylphenyl.

R^1 to R^{10} each independently represent C_1 to C_6 alkyl, phenyl or C_1 to C_6 alkylphenyl.

10 Further preferred compounds of formula (I) include those wherein:

A and B both represent $-CH_2-$ or C_2H_4 , particularly CH_2 ;

15 K, D, Z and E each independently represent hydrogen, C_1 - C_6 alkyl phenyl or C_1 - C_6 alkyl or $-J-Q^3(CR^{13}(R^{14})(R^{15}))CR^{16}(R^{17})(R^{18})$ where J is the same as A; or two of K, D, E and Z together with the carbon atoms of the aryl ring to which they are attached form an unsubstituted
20 phenyl ring;

R^1 to R^{18} each independently represent C_1 to C_6 alkyl;

Still further preferred compounds of formula (I) include
25 those wherein:

R^1 to R^{18} are the same and each represents C_1 to C_6 alkyl, particularly methyl.

30 Still further preferred compounds of formula I include those wherein:

K, D, Z and E are each independently selected from the group consisting of hydrogen or C₁ to C₆ alkyl, particularly where each of K, D, Z and E represent the same group, especially where each of K, D, Z and E
5 represent hydrogen; or

K represents $-\text{CH}_2-\text{Q}^3(\text{CR}^{13}(\text{R}^{14})(\text{R}^{15}))\text{CR}^{16}(\text{R}^{17})(\text{R}^{18})$ and D, Z and E are each independently selected from the group consisting of hydrogen or C₁ to C₆ alkyl, particularly
10 where both D and E represent the same group, especially where D, Z and E represent hydrogen.

Especially preferred specific compounds of formula (I) include those wherein:

15

each R¹ to R¹² is the same and represents methyl;
A and B are the same and represent $-\text{CH}_2-$;
K, D, Z and E are the same and represent hydrogen.

20 The present invention provides a process for the hydroformylation of an ethylenically unsaturated compound comprising contacting an ethylenically unsaturated compound with carbon monoxide and hydrogen in the presence of a catalyst system and solvent as defined in the present
25 invention.

Suitably, the hydroformylation reaction is carried out at a temperature of between 20°C and 180°C, more preferably 35°C and 165°C, most preferably 50°C to 150°C and under a
30 partial pressure of carbon monoxide/hydrogen in the range of 1 to 700 bar, preferably 1 to 600 bar, more preferably 1 to 300 bar.

Suitably, the ethylenically unsaturated compound may include more than one carbon-carbon double bond, wherein the double bonds are conjugated or non-conjugated.

- 5 Preferably, the ethylenically unsaturated compound has 1 to 3 carbon-carbon double bonds per molecule, particularly only 1 or 2 carbon-carbon double bonds per molecule, generally only 1 carbon-carbon double bond per molecule.
- 10 In the process according to the present invention, the carbon monoxide and hydrogen may be used either in pure form or diluted with an inert gas such as nitrogen, carbon dioxide or a noble gas such as argon.
- 15 The amount of the catalyst of the invention used in the hydroformylation process of the ethylenically unsaturated compound is not critical. Good results may be obtained when, preferably, the amount of Group VIII metal is in the range 10^{-7} to 10^{-1} moles per mole of ethylenically
- 20 unsaturated compound, more preferably, 10^{-6} to 10^{-2} moles, most preferably 10^{-3} to 10^{-2} moles per mole of ethylenically unsaturated compound. Preferably, the amount of bidentate compound of formula (I) to unsaturated compound is in the range 10^{-7} to 10^{-1} , more preferably, 10^{-6}
- 25 to 10^{-2} , most preferably, 10^{-5} to 10^{-2} moles per mole of ethylenically unsaturated compound.

The catalyst compounds of the present invention may act as a "heterogeneous" catalyst or a "homogeneous" catalyst.

30

By the term "homogeneous" catalyst we mean a catalyst, i.e. a compound of the invention, which is not supported but is simply admixed or formed in-situ with the reactants

of the hydroformylation reaction (e.g. the ethylenically unsaturated compound, hydrogen and carbon monoxide), preferably in a suitable solvent as described herein.

- 5 By the term "heterogeneous" catalyst we mean a catalyst, i.e. the compound of the invention, which is carried on a support.

Thus according to a further aspect, the present invention
10 provides a process for the hydroformylation of ethylenically unsaturated compounds as defined herein wherein the process is carried out with the catalyst comprising a support, preferably an insoluble support.

- 15 Preferably, the support comprises a polymer such as a polyolefin, polystyrene or polystyrene copolymer such as a divinylbenzene copolymer or other suitable polymers or copolymers known to those skilled in the art; a silicon derivative such as a functionalised silica, a silicone or
20 a silicone rubber; or other porous particulate material such as for example inorganic oxides and inorganic chlorides.

Preferably the support material is porous silica which has
25 a surface area in the range of from 10 to 700 m²/g, a total pore volume in the range of from 0.1 to 4.0 cc/g and an average particle size in the range of from 10 to 500 μm. More preferably, the surface area is in the range of from 50 to 500 m²/g, the pore volume is in the range of from
30 0.5 to 2.5 cc/g and the average particle size is in the range of from 20 to 200 μm. Most desirably, the surface area is in the range of from 100 to 400 m²/g, the pore volume is in the range of from 0.8 to 2.0 cc/g and the

average particle size is in the range of from 30 to 100 μm . The average pore size of typical porous support materials is in the range of from 10 to 1000 Å. Preferably, a support material is used that has an average pore diameter of from 50 to 500 Å, and most desirably from 75 to 350 Å. It may be particularly desirable to dehydrate the silica at a temperature of from 100°C to 800°C anywhere from 3 to 24 hours.

10 Suitably, the support may be flexible or rigid and the insoluble support is coated and/or impregnated with the compounds of the process of the invention by techniques well known to those skilled in the art.

15 Alternatively, the compounds of the process of the invention are fixed to the surface of an insoluble support, optionally via a covalent bond, and the arrangement optionally includes a bifunctional spacer molecule to space the compounds from the insoluble
20 support.

The compounds of the invention may be fixed to the surface of the insoluble support by promoting reaction of a functional group present in the compound of formula (I),
25 for example a substituent K, D, Z and E of the aryl moiety, with a complimentary reactive group present on or previously inserted into the support. The combination of the reactive group of the support with a complimentary substituent of the compound of the invention provides a
30 heterogeneous catalyst where the compound of the invention and the support are linked via a linkage such as an ether, ester, amide, amine, urea, keto group.

The choice of reaction conditions to link a compound of the process of the present invention to the support depends upon the nature of the substituents(s) of the compound and the groups of the support. For example, reagents such as carbodiimides, 1,1'-carbonyldiimidazole, and processes such as the use of mixed anhydrides, reductive amination may be employed.

According to a further aspect, the present invention provides the use of the process of the invention wherein the catalyst is attached to a support.

Particularly preferred is when the organic groups R^1 , R^2 , R^3 , R^4 , R^5 , R^6 , R^7 , R^8 , R^9 , R^{10} , R^{11} and R^{12} when associated with their respective carbon atom form composite groups which are at least as sterically hindering as t-butyl. Steric hindrance in this context is as discussed at page 14 et seq of "Homogenous Transition Metal Catalysis - A Gentle Art", by C Masters, published by Chapman and Hall 1981.

The bridging group Ar is an aryl moiety, e.g. a phenyl group, which may be optionally substituted, provided that the two phosphorus atoms are linked to adjacent carbon atoms, e.g. at the 1 and 2 positions on the phenyl group. Furthermore, the aryl moiety may be a fused polycyclic group, e.g. naphthalene, biphenylene or indene.

Examples of suitable bidentate ligands are bis (di-t-butyl phosphino)-o-xylene (also known as 1,2 bis (di-t-butylphosphinomethyl) benzene); 1,2 bis (diadamantylphosphinomethyl) benzene; 1,2 bis (diadamantylphosphinomethyl) naphthalene; 1,2 bis (di-t-

pentylphosphino)-o-xylene (also known as 1,2 bis (di-t-pentyl-phosphinomethyl) benzene); and bis 1,2 (di-t-butyl phosphinomethyl) naphthalene. Additionally, the bidentate phosphine may be bonded to a suitable polymeric substrate via at least one of the bridging group Ar, the linking group A or the linking group B, e.g. bis (di-t-butyl phosphino)-o-xylene may be bonded via the xylene group to polystyrene to give an immobile heterogeneous catalyst.

- 10 The amount of bidentate ligand used can vary within wide limits. Preferably, the bidentate ligand is present in an amount such that the ratio of the number of moles of the bidentate ligand present to the number of moles of the Group VIII metal present is from 1 to 50, e.g. from 1 to 10, and particularly from 1 to 5, mol per mol of metal. More preferably, the mol:mol range of compounds of formula (I) to Group VIII metal is in the range of 1:1 to 3:1, most preferably in the range of 1:1 to 1.25:1. Conveniently, the possibility of applying these low molar ratios is advantageous, as it avoids the use of an excess of the compound of formula (I) and hence minimises the consumption of these usually quite expensive compounds. Suitably, the catalysts of the process of the invention are prepared in a separate step preceding their use in-situ in the hydroformylation reaction of an ethylenically unsaturated compound.

The carbon monoxide and hydrogen may be used in the presence of other gases which are inert in the reaction. Examples of such gases include nitrogen, carbon dioxide and the noble gases such as argon.

- Suitable Group VIII metals or a compound thereof which may be combined with a compound of formula (I) include cobalt, nickel, palladium, rhodium, ruthenium and platinum. Preferably, (a) is rhodium or a compound thereof. Suitable
- 5 compounds of such Group VIII metals include salts of such metals with, or compounds comprising weakly coordinated anions derived from, nitric acid; sulphuric acid; lower alkanolic (up to C_{12}) acids such as acetic acid and propionic acid; sulphonic acids such as methane sulphonic
- 10 acid, chlorosulphonic acid, fluorosulphonic acid, trifluoromethane sulphonic acid, benzene sulphonic acid, naphthalene sulphonic acid, toluene sulphonic acid, e.g. p-toluene sulphonic acid, t-butyl sulphonic acid, and 2-hydroxypropane sulphonic acid; sulphonated ion exchange
- 15 resins; perhalic acid such as perchloric acid; halogenated carboxylic acids such as trichloroacetic acid and trifluoroacetic acid; orthophosphoric acid; phosphonic acids such as benzenephosphonic acid; and acids derived from interactions between Lewis acids and Brønsted acids.
- 20 Other sources which may provide suitable anions include the optionally halogenated tetraphenyl borate derivatives, e.g. perfluorotetraphenyl borate. Of course, the process of the invention requires the presence of a chlorine moiety in at least one of the Group VIII metal compound or
- 25 the solvent, and therefore should the solvent not contain a chlorine moiety, the Group VIII metal compound must contain a chlorine moiety, and the foregoing is to be read accordingly.
- 30 The catalyst system of the present invention is preferably constituted in the liquid phase which may be formed by one or more of the reactants or by the use of a suitable solvent. Clearly, in the former case, the references to

solvent in the present invention should be construed accordingly and the chlorine moiety must, in such cases, be present in the Group VIII metal compound.

- 5 The choice of solvent is not critical, aside from the fact that according to the invention, it must comprise a chlorine moiety if the Group VIII metal compound does not. Naturally, the solvent chosen should not be detrimental to either the catalyst system, reactants or products.
- 10 Moreover, the solvent can be a mixture of reactants, such as the ethylenically unsaturated compound, the product and/or any by-products, and the higher-boiling products of secondary reactions thereof, e.g. aldol condensation products.
- 15 Suitable solvents, when present, include saturated hydrocarbons such as kerosene, mineral oil or cyclohexane, ethers such as diphenyl ether, methyl phenyl ether, diethylether, diisopropylether, tetrahydrofuran or a
- 20 polyglycol, ketones such as acetone, methyl ethyl ketone, methyl butyl ketone and cyclohexanone, nitriles such as methylglutaronitrile, valeronitrile, and benzonitrile, aromatics, including halo variants, such as toluene, benzene and xylene, esters such as methylacetate,
- 25 methylvalerate and caprolactone, dimethylformamide, and sulfones such as tetramethylenesulfone, and variants of any of the aforesaid comprising at least one chlorine moiety.
- 30 Other suitable solvents include aromatic compounds such as toluene (as noted above), hydrocarbons or mixtures of hydrocarbons. It is also possible to use water, and alcohols such as methanol, ethanol, n-propanol,

isopropanol, n-butanol and isobutanol. Variants of the aforesaid comprising at least one chlorine moiety are also suitable.

- 5 As noted hereinbefore, a chlorine moiety is present in at least one of the Group VIII metal compound or solvent of the process of the invention. Thus, suitably, the Group VIII metal compound is as defined hereinbefore and comprising a chlorine moiety. Specific examples of
- 10 suitable rhodium complexes (both those with and those without at least one chlorine moiety) include $[\text{RhCl}(\text{CO})_2]_2$, $[\text{RhCl}(\text{Cod})_2]_2$, $\text{RhCl}_3 \cdot x\text{H}_2\text{O}$, $[\text{Rh}(\text{CO})_2(\text{acac})]$, $[\text{Rh}(\text{acetate})_2]_2$, $[\text{RhCl}(\text{Norbornadiene})]_2$, $\text{Rh}_2(\text{OAc})_4$, $[\text{RhCl}(\text{Cyclooctene})_2]_2$, Chloro(1,5-hexadiene)-
- 15 rhodium(I)dimer, Bis(1,5-cyclooctadiene)-rhodium(I)tetrafluoroborate hydrate, Mu-dichlorotetraethylene-dirhodium, (bicyclo[2,2,1]hepta-2-5-diene)chlororhodium(I)dimer, (1,5-cyclooctadiene)(2,4-pentanedionato)rhodium(I), (bicyclo[2,2,1]hepta-2-5-
- 20 diene)(2,4-pentanedionato)rhodium(I), rhodium(III)acetylacetonate, (bicyclo[2,2,1]hepta-2-5-diene)chlororhodium(I)dimer, more especially $[\text{RhCl}(\text{CO})_2]_2$, $[\text{RhCl}(\text{Cod})_2]_2$, $\text{RhCl}_3 \cdot x\text{H}_2\text{O}$, $[\text{Rh}(\text{CO})_2(\text{acac})]$, $[\text{Rh}(\text{acetate})_2]_2$, $[\text{RhCl}(\text{Norbornadiene})]_2$, $[\text{RhCl}(\text{Cyclooctene})_2]_2$, Chloro(1,5-
- 25 hexadiene)-rhodium(I)dimer, most especially $[\text{RhCl}(\text{CO})_2]_2$, $[\text{RhCl}(\text{Cod})_2]_2$, $\text{RhCl}_3 \cdot x\text{H}_2\text{O}$, $[\text{Rh}(\text{CO})_2(\text{acac})]$, $[\text{Rh}(\text{acetate})_2]_2$. Thus, where the rhodium complexes are to comprise at least one chlorine moiety, suitable complexes include $[\text{RhCl}(\text{CO})_2]_2$, $[\text{RhCl}(\text{Cod})_2]_2$, $\text{RhCl}_3 \cdot x\text{H}_2\text{O}$, $[\text{RhCl}(\text{Norborn-}$
- 30 adiene)]₂, $[\text{RhCl}(\text{Cyclooctene})_2]_2$, Chloro(1,5-hexadiene)-rhodium(I)dimer, Mu-dichlorotetraethylene-dirhodium, (bicyclo[2,2,1]hepta-2-5-diene)chlororhodium(I)dimer, more especially $[\text{RhCl}(\text{CO})_2]_2$, $[\text{RhCl}(\text{Cod})_2]_2$, $\text{RhCl}_3 \cdot x\text{H}_2\text{O}$,

[RhCl(Norbornadiene)]₂, [RhCl(Cyclooctene)]₂, Chloro(1,5-hexadiene)-rhodium(I)dimer, most especially [RhCl(CO)]₂, [RhCl(Cod)]₂, RhCl₃·xH₂O. Moreover, suitably, the solvent of the process of the invention is as defined hereinbefore and comprising a chlorine moiety. Specific examples of such solvents comprising at least one chloro moiety include dichloromethane, chlorobenzene, o-dichlorobenzene, m-chlorobenzene, carbon tetrachloride, trichloroethanes, dichloroethanes, chlorofluorocarbons (CFC's), tetrachloroethanes, tetrachloroethene, more especially dichloromethane. Even more preferably, both the Group VIII metal compound and the solvent contain a chlorine moiety.

The product of the reaction may be separated from the other components by any suitable means. However, it is an advantage of the present process that significantly fewer by-products are formed thereby reducing the need for further purification after the initial separation of the product as may be evidenced by the generally significantly higher selectivity and linearity. A further advantage is that the other components which contain the catalyst system may be recycled and/or reused in further reactions with minimal supplementation of fresh catalyst.

25

Preferably, the hydroformylation is carried out at a temperature of between 20°C and 180°C, more preferably 35°C and 165°C, most preferably 50°C to 150°C. Advantageously, the hydroformylation can be carried out at moderate temperatures. It is particularly advantageous to be able to carry out the hydroformylation reaction at above room temperature.

Suitably, the hydroformylation is carried out at the partial pressure of the reaction gas mixture at the chosen reaction temperature. Generally, the partial pressure is in the range of 1 to 700 bar, preferably 1 to 600 bar, more preferably 1 to 300 bar. However, the partial pressure may be varied from these ranges depending on the activity of the hydroformylation catalyst employed. In the case of catalyst systems of the present invention, for example, reaction would also proceed in a low-pressure region, for example in the range 1 to 100 bar.

The reaction may be carried out on any ethylenically unsaturated compound including ethylene although there is no linearity advantage as such with ethylene. Preferably, the reaction is therefore suitable for C_3 - C_{20} ethylenically unsaturated compounds, more preferably, C_3 - C_{18} , most preferably C_3 - C_{12} compounds.

The process may be carried out on ethylenically unsaturated compounds having 2 or more carbon atoms such as C_2 - C_{10} atoms or C_3 - C_{20} atoms or C_4 - C_{20} atoms. The alternative upper range of carbon atoms in such compounds may be taken as C_{18} or C_{15} or C_{12} in increasing order of preference. The alternative lower range of carbon atoms in any of the aforesaid ranges of ethylenically unsaturated compounds may be C_3 , C_4 , C_5 or C_6 . The ethylenically unsaturated compound is, preferably, an alkene having 1, 2 or 3 or more carbon-carbon double bonds per molecule.

Any such alkene can be substituted or non-substituted. Suitable substituents include C_{1-3} alkyl and C_{1-2} aryl groups. Unless otherwise specified, the ethylenically

unsaturated compound may, when there are sufficient number of carbon atoms, be linear or branched, be substituted, be cyclic, acyclic or part cyclic/acyclic, and/or be optionally substituted or terminated by one or more substituents selected from lower alkyl, aryl, alkylaryl, Het, alkylHet, halo, OR^{19} , $OC(O)R^{20}$, $C(O)R^{21}$, $C(O)OR^{22}$, $NR^{23}R^{24}$, $C(O)NR^{25}R^{26}$, NO_2 , CN , SR^{27} wherein R^{19} to R^{27} each independently represent hydrogen or lower alkyl. Olefins thus substituted include styrene and alkyl esters of unsaturated carboxylic acids, such as methacrylate. Suitably, the ethylenically unsaturated compound may exhibit cis (E) and trans (Z) isomerism.

Examples of suitable ethylenically unsaturated compounds may be independently selected from ethene, propene, 1-butene, 2-butene, isobutene, 1-pentene, 2-pentene, 3-pentene and branched isomers thereof, 1-hexene and its isomers, 1-heptene and its isomers, 1-octene and its isomers, 1-nonene and its isomers, 1-decene and its isomers, the C_{11} - C_{20} alkenes and their known isomers, 3-pentenitrile, methyl-3-penteneoate, 1,3 butadiene, 1,3-pentadiene, 1,3 hexadiene, 1,3 cyclohexadiene, 2,4-leptadiene, and 2-methyl 1,3 butadiene.

The following non-limiting and purely illustrative examples further illustrate the present invention.

All syntheses were carried out in a vacuum-argon Schlenk line using dried and degassed Schlenk glassware.

1-octene and 1-hexene (both from Aldrich) were purified by distillation and degassed by bubbling with argon. Toluene was dried by distillation from sodium diphenyl ketal. THF

(tetrahydrofuran) was dried by distillation with sodium and benzophenone. DCM (dichloromethane) was dried by distillation with calcium hydride.

5 [RhCl(CO)₂]₂, Rh₂(OAc)₄, and RhCl₃.xH₂O (Strem) were stored in a glove box due to their air-sensitive nature. 1,2-bis(di-tertbutylphosphinomethyl)benzene was also stored and handled in a glove box due to its air-sensitive nature.

10 The catalytic solutions were made up as follows.

For catalytic systems having [RhCl(CO)₂]₂ as rhodium precursor, 9mg (0.023mmol) of [RhCl(CO)₂]₂ and 20mg (0.046mmol) of 1,2-bis(di-tertbutylphosphinomethyl)benzene
15 were added to a Schlenk tube in a glove box. The corresponding solvent (typically 10ml) was then added with a syringe. When all the solids were dissolved, 1-octene or 1-hexene (2ml), the substrate for hydroformylation, was added to the solution.

20

The autoclaves used for these examples were 250ml hastelloy autoclaves. After being dried in an oven, the autoclave was flushed three times with argon. Once it was degassed, the solution was transferred via canula. Then
25 it was pressured with 30bar of synthesis gas and heated to 80°C for 3hrs, after which it was cooled in air and then vented. The solutions obtained were analysed with GC-MS.

The catalytic systems in which either Rh₂(OAc)₄ or RhCl₃,
30 were used as rhodium precursors, were prepared following the same procedure as that outlined above.

The percentage conversion is an expression of the amount of substrate converted by the reaction.

The selectivity is a measure of the selectivity to the particular hydroformylated product.

1:b is a representation of the linear:branched ratio of the hydroformylated products.

10 Example 1

Hydroformylation of 1-hexene: Chlorine moiety present in rhodium precursor

9.0 mg (0.00383mol/litre) of $[\text{RhCl}(\text{CO})_2]_2$ was added to 18 mg (0.00383mol/litre) of the bidentate phosphine ligand, 1,2-bis(di-tertbutylphosphinomethyl)benzene. 10ml of toluene was then added to the mixture. 2.0 ml (16.0mmol) of 1-hexene was then added and hydroformylation was performed for 3hrs by the addition, at 80°C, of a 1:1 mixture of $\text{CO}:\text{H}_2$ at a pressure of 30bar.

It was found that after 3hrs under these conditions, there was 100% conversion of 1-hexene to the aldehyde product, with 84% selectivity to linear heptanal over the branched product, an 1:b ratio of 5.25:1.

Comparative Example 1

Hydroformylation of 1-hexene: Chlorine moiety not present

10 mg (0.00383mol/litre) of $[\text{Rh}(\text{OAc})_2]_2$ was added to 40 mg (0.00846mol/litre) of the bidentate phosphine ligand, 1,2-bis(di-tertbutylphosphinomethyl)benzene. 10ml of toluene was then added to the mixture. 2.0ml (16.0mmol) of 1-

hexene was then added and hydroformylation was performed for 3hrs by the addition, at 80°C, of a 1:1 mixture of CO:H₂ at a pressure of 30bar.

- 5 It was found that after 3hrs under these conditions, there was 100% conversion of 1-hexene to the aldehyde product, with 55% selectivity to linear heptanal over the branched product, an 1:b ratio of only 1.22:1.
- 10 Comparative Example 1 and Example 1 clearly show the increase in selectivity towards the linear product over the branched product, from the hydroformylation of 1-hexene, when chlorine moiety is present in the rhodium compound precursor to the catalyst system compared with
- 15 when the chlorine moiety is not present.

Example 2

Hydroformylation of allyl alcohol: Chlorine moiety present in rhodium precursor

- 20 9.0 mg (0.00383mol/litre) of [RhCl(Cod)₂]₂ was added to 18.0 mg (0.00383mol/litre) of the bidentate phosphine ligand, 1,2-bis(di-tertbutylphosphinomethyl)benzene. 10ml of toluene was then added to the mixture. 2.0 ml
- 25 (29.0mmol) of allyl alcohol was then added and hydroformylation was performed for 3hrs by the addition, at 80°C, of a 1:1 mixture of CO:H₂ at a pressure of 30bar, and in the presence of 0.072mmol of NaOAc.
- 30 It was found that after 3hrs under these conditions, there was 86.6% conversion of allyl alcohol, with 73.8% selectivity to hydroxytetrahydrofuran, 12.9% to hydroxymethyl-propionaldehyde. These two products were

then hydrogenated to give, respectively, 1,4-butanediol and 2-methyl-1,3-propanediol. The 1:b ratio in this case was 5.72:1.

5 Example 3

Hydroformylation of allyl alcohol: Chlorine moiety present in solvent

Example 2 was repeated but in this case, the rhodium compound was $[\text{Rh}(\text{OAc})_2]_2$ and the solvent used was dichloromethane.

In this case, there was 100% conversion of allyl alcohol, with 75% selectivity to hydroxytetrahydrofuran, 17% hydroxymethylpropionaldehyde, giving hydrogenated products in the 1:b ratio 4.41:1.

Examples 2 and 3 show the relatively high selectivity towards the linear as opposed to the branched product, from the hydroformylation of allyl alcohol, when chlorine moiety is present in the rhodium compound precursor to the catalyst system (Example 2) or in the solvent (Example 3).

Example 4

25 Hydroformylation of 1-octene: Chlorine moiety present in solvent

5.0 mg (0.0016mol/litre) of $[\text{Rh}(\text{acac})(\text{CO})_2]_2$ was added to 18.0 mg (0.00383mol/litre) of the biphosphine ligand, 1,2-bis(di-tertbutylphosphinomethyl)benzene. 10ml of dichloromethane was then added to the mixture. 2.5 ml (16mmol) of 1-octene was then added and hydroformylation

was performed for 3hrs by the addition, at 80°C, of a 1:1 mixture of CO:H₂ at a pressure of 30bar.

It was found that after 3hrs under these conditions, there
5 was 29% conversion to the aldehyde product, with 80% selectivity to linear nonanal over the branched product, an 1:b ratio of 4:1.

Example 5

10 Hydroformylation of 1-octene: Chlorine moiety present in rhodium precursor and in solvent

Details were as in Example 4 above, except 9.0 mg
(0.00383mol/litre) of [RhCl(CO)₂]₂ was used as the rhodium
15 precursor.

Once again, it was found that there was 29% conversion to the aldehyde product, with 80% selectivity to linear nonanal over the branched product, an 1:b ratio of 4:1.

20

Example 6

Hydroformylation of 1-octene: Chlorine moiety present in rhodium precursor

25 Details were as in Example 5 above, except 10ml of OctMIMTfN was used as the solvent.

In this case, it was found that there was 10% conversion to the aldehyde product, with 80% selectivity to linear
30 nonanal over the branched product, an 1:b ratio of 4:1.

Example 75 Hydroformylation of 1-octene: Chlorine moiety present in rhodium precursor

Details were as in Example 5 above, except 10ml of toluene was used as the solvent.

10

In this case, it was found that there was 11% conversion to the aldehyde product, with 100% selectivity to linear nonanal.

15 Comparative Example 2Hydroformylation of 1-octene: Chlorine moiety not present

Details were as in Example 4 above, except 10ml of toluene was used as the solvent.

20

In this case, it was found that there was 89% conversion to the aldehyde product, with only 50% selectivity to linear nonanal, an 1:b ratio of 1:1.

25 Examples 4-7 clearly show the increase in selectivity towards the linear product over the branched product, from the hydroformylation of 1-octene, when chlorine moiety is present in the solvent (Example 4), the rhodium precursor (Examples 6 and 7), or both the solvent and the rhodium
30 precursor (Example 5), compared to Comparative Example 2, where no chlorine moiety is present, either in the rhodium precursor or in the solvent.

The reader's attention is directed to all papers and documents which are filed concurrently with or previous to this specification in connection with this application and which are open to public inspection with this specification, and the contents of all such papers and documents are incorporated herein by reference.

All of the features disclosed in this specification (including any accompanying claims, abstract and drawings), and/or all of the steps of any method or process so disclosed, may be combined in any combination, except combinations where at least some of such features and/or steps are mutually exclusive.

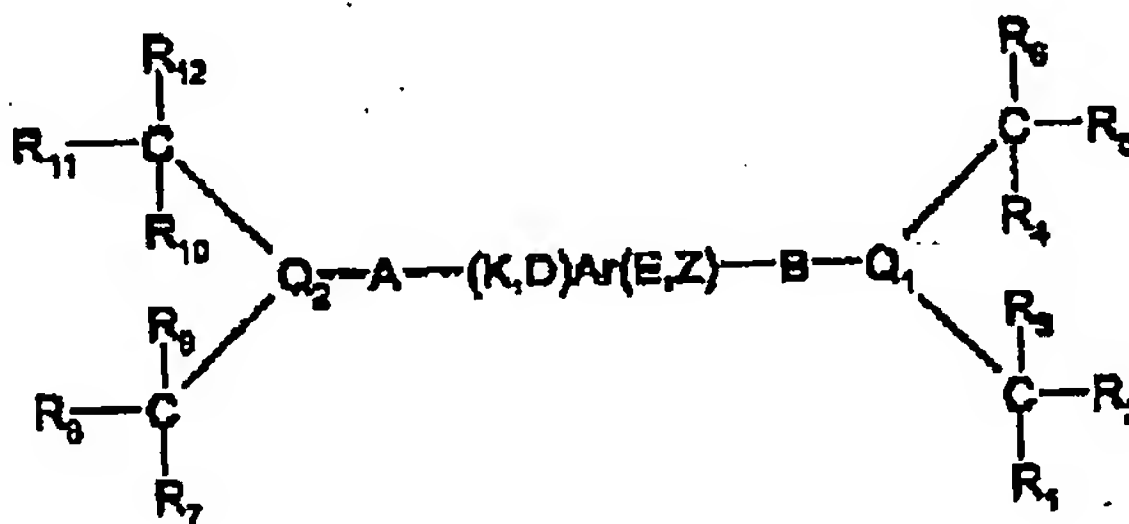
Each feature disclosed in this specification (including any accompanying claims, abstract and drawings), may be replaced by alternative features serving the same, equivalent or similar purpose, unless expressly stated otherwise. Thus, unless expressly stated otherwise, each feature disclosed is one example only of a generic series of equivalent or similar features.

The invention is not restricted to the details of the foregoing embodiment(s). The invention extends to any novel one, or any novel combination, of the features disclosed in this specification (including any accompanying claims, abstract and drawings), or to any novel one, or any novel combination, of the steps of any method or process so disclosed.

According to the present invention there is provided a process for the hydroformylation of ethylenically unsaturated compounds, as set forth in the appended claims. Preferred features of the invention will be apparent from the dependent claims, and the description.

CLAIMS

1. A process for the hydroformylation of ethylenically unsaturated compounds, which process comprises reacting said ethylenically unsaturated compound with carbon monoxide and hydrogen, in the presence of a catalyst system, the catalyst system obtainable by combining:
- 5
- 10 a) a metal of Group VIII or a compound thereof; and
- b) a bidentate phosphine of general formula (I)



wherein:

- 15 Ar is a bridging group comprising an optionally substituted aryl moiety to which the phosphorus atoms are linked on available adjacent carbon atoms;

A and B each independently represent lower alkylene;

- 20 K, D, E and Z are substituents of the aryl moiety (Ar) and each independently represent hydrogen, lower alkyl, aryl, Het, halo, cyano, nitro, OR¹⁹, OC(O)R²⁰, C(O)R²¹, C(O)OR²², NR²³R²⁴, C(O)NR²⁵R²⁶, C(S)R²⁵R²⁶, SR²⁷, C(O)SR²⁷, or -J-Q³(CR¹³(R¹⁴)(R¹⁵))CR¹⁶(R¹⁷)(R¹⁸) where J represents lower alkylene; or two adjacent groups
- 25

selected from R, Z, D and E together with the carbon atoms of the aryl ring to which they are attached form a further phenyl ring, which is optionally substituted by one or more substituents selected from
5 hydrogen, lower alkyl, halo, cyano, nitro, OR^{19} , $OC(O)R^{20}$, $C(O)R^{21}$, $C(O)OR^{22}$, $NR^{23}R^{24}$, $C(O)NR^{25}R^{26}$, $C(S)R^{25}R^{26}$, SR^{27} or $C(O)SR^{27}$;

10 R^1 to R^{18} each independently represent lower alkyl, aryl, or Het;

R^{19} to R^{27} each independently represent hydrogen, lower alkyl, aryl or Het;

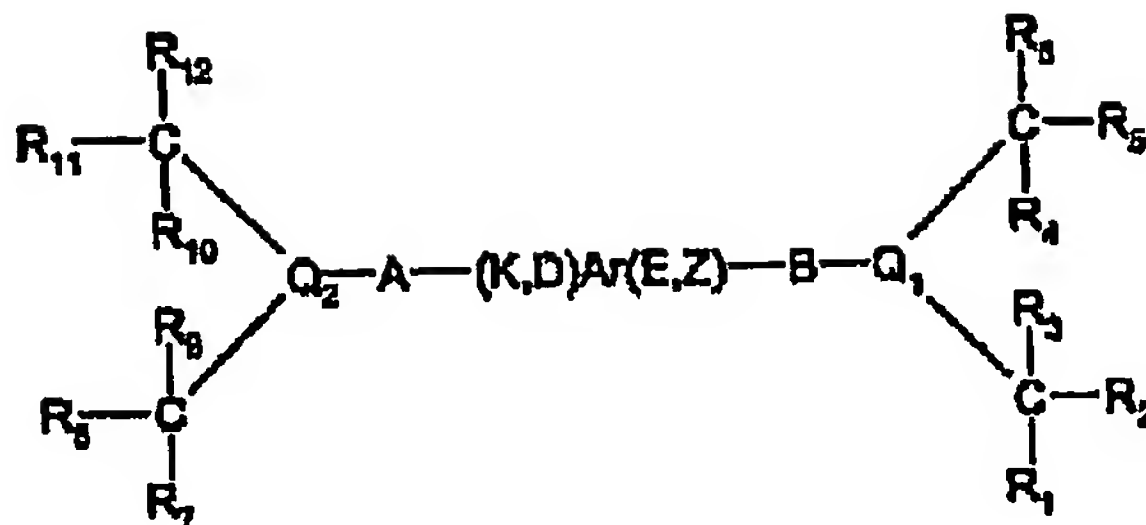
15 Q^1 , Q^2 and Q^3 (when present) each independently represent phosphorous, arsenic or antimony and in the latter two cases references to phosphine or phosphorous above are amended accordingly.

20 the process characterised in that a chlorine moiety is present in at least said Group VIII metal compound.

2. A process for the hydroformylation of ethylenically
25 unsaturated compounds, which process comprises reacting said ethylenically unsaturated compound with carbon monoxide and hydrogen, in the presence of a catalyst system and a solvent, the catalyst system obtainable by combining:

30

- a) a metal of Group VIII or a compound thereof; and
- b) a bidentate phosphine of general formula (I)



wherein:

Ar is a bridging group comprising an optionally substituted aryl moiety to which the phosphorus atoms are linked on available adjacent carbon atoms;

A and B each independently represent lower alkylene;

K, D, E and Z are substituents of the aryl moiety (Ar) and each independently represent hydrogen, lower alkyl, aryl, Het, halo, cyano, nitro, OR¹⁹, OC(O)R²⁰, C(O)R²¹, C(O)OR²², NR²³R²⁴, C(O)NR²⁵R²⁶, C(S)R²⁵R²⁶, SR²⁷, C(O)SR²⁷, or -J-Q³(CR¹³(R¹⁴)(R¹⁵))CR¹⁶(R¹⁷)(R¹⁸) where J represents lower alkylene; or two adjacent groups selected from K, Z, D and E together with the carbon atoms of the aryl ring to which they are attached form a further phenyl ring, which is optionally substituted by one or more substituents selected from hydrogen, lower alkyl, halo, cyano, nitro, OR¹⁹, OC(O)R²⁰, C(O)R²¹, C(O)OR²², NR²³R²⁴, C(O)NR²⁵R²⁶, C(S)R²⁵R²⁶, SR²⁷ or C(O)SR²⁷,

R¹ to R¹⁸ each independently represent lower alkyl, aryl, or Het;

R¹⁹ to R²⁷ each independently represent hydrogen, lower alkyl, aryl or Het;

5 Q¹, Q² and Q³ (when present) each independently represent phosphorous, arsenic or antimony and in the latter two cases references to phosphine or phosphorous above are amended accordingly,

10 the process characterised in that a chlorine moiety is present in at least one of the said Group VIII metal compound or said solvent.

15 3. The process as claimed in claim 2, wherein a chlorine moiety is present in both said Group VIII metal compound and said solvent.

20 4. The process as claimed in any of claims 1 to 3, wherein R¹ to R¹⁸ each independently represent C₁ to C₆ alkyl, C₁ to C₆ alkyl phenyl or phenyl.

25 5. The process as claimed in claim 4, wherein R¹ to R¹⁸ each independently represent methyl, ethyl, n-propyl, iso-propyl, n-butyl, iso-butyl, tert-butyl, pentyl, hexyl and cyclohexyl.

30 6. The process as claimed in any preceding claim, wherein R¹, R⁴, R⁷, R¹⁰, R¹³ and R¹⁶ each independently represent the same C₁-C₆ alkyl; R², R⁵, R⁸, R¹¹, R¹⁴ and R¹⁷ each independently represent the same C₁₋₆ alkyl; and R³, R⁶, R⁹, R¹², R¹⁵ and R¹⁸ each independently represent the same C₁₋₆ alkyl.

7. The process as claimed in any preceding claim, wherein R^1 to R^{18} each represents the same C_1 - C_6 alkyl group.
- 5 8. The process as claimed in claim 7, wherein the said C_1 - C_6 alkyl group is non-substituted and selected from the list comprising: methyl, ethyl, n-propyl, iso-propyl, n-butyl, iso-butyl, tert-butyl, pentyl, hexyl and cyclohexyl.
- 10 9. The process as claimed in claim 8, wherein the said C_1 - C_6 alkyl group is methyl.
- 15 10. The process as claimed in any preceding claim, wherein Q^1 , Q^2 and Q^3 (when present) represents phosphorus.
- 20 11. The process as claimed in any preceding claim, wherein A, B and J (when present) each independently represent C_1 to C_6 alkylene.
12. The process as claimed in claim 11, wherein each of A, B and J (when present) represent $-CH_2-$.
- 25 13. The process as claimed in any preceding claim, wherein K, D, E and Z each represent hydrogen, phenyl, C_1 - C_6 alkylphenyl or C_1 - C_6 alkyl.
- 30 14. The process as claimed in claim 13, wherein K, D, E and Z each represent hydrogen.
15. The process as claimed in any of claims 1 to 3, wherein in formula (I):

A and B each independently represent unsubstituted C₁ to C₆ alkylene;

5 K, D, Z and E each independently represent hydrogen, C₁-C₆ alkyl, phenyl, C₁-C₆ alkylphenyl or -J-Q³(CR¹³(R¹⁴)(R¹⁵))CR¹⁶(R¹⁷)(R¹⁸) where J represents unsubstituted C₁ to C₆ alkylene; or two of K, D, Z and E together with the carbon atoms of the aryl ring
10 to which they are attached form a phenyl ring which is optionally substituted by one or more substituents selected from lower alkyl, phenyl or lower alkylphenyl;

15 R¹ to R¹⁸ each independently represent C₁ to C₆ alkyl, phenyl or C₁ to C₆ alkylphenyl.

16. The process as claimed in any of claims 1 to 3, wherein in formula (I):

20

A and B both represent -CH₂- or C₂H₄;

K, D, Z and E each independently represent hydrogen, C₁-C₆ alkyl phenyl or C₁-C₆ alkyl or -J-Q³(CR¹³(R¹⁴)(R¹⁵))CR¹⁶(R¹⁷)(R¹⁸) where J is the same as
25 A; or two of K, D, E and Z together with the carbon atoms of the aryl ring to which they are attached form an unsubstituted phenyl ring;

30 R¹ to R¹⁸ each independently represent C₁ to C₆ alkyl;

17. The process as claimed in claim 16, wherein A and B both represent -CH₂-.

18. The process as claimed in any of claims 1 to 3,
wherein in formula (I):

5 each R¹ to R¹² is the same and represents methyl;
A and B are the same and represent -CH₂-;
K, D, Z and E are the same and represent hydrogen.

10 19. The process as claimed in any preceding claim,
wherein the reaction is carried out at a temperature
of between 20°C and 180°C.

20. The process as claimed in claim 19, wherein the
temperature is in the range 50°C to 150°C.

15 21. The process as claimed in any preceding claim,
wherein the reaction is carried out under a partial
pressure of carbon monoxide/hydrogen in the range of
1 to 700 bar.

20 22. The process as claimed in claim 21, wherein the
partial pressure is in the range 1 to 300 bar.

25 23. The process as claimed in any preceding claim,
wherein said ethylenically unsaturated compound has 1
to 3 carbon-carbon double bonds per molecule.

30 24. The process as claimed in claim 23, wherein said
compound has 1 carbon-carbon double bond per
molecule.

25. The process as claimed in any preceding claim,
wherein the amount of bidentate compound of formula

(I) to unsaturated compound is in the range 10^{-5} to 10^{-2} moles per mole of unsaturated compound.

5 26. The process as claimed in any preceding claim, wherein said catalyst system further comprises a support.

10 27. The process as claimed in any preceding claim, wherein said bidentate phosphine is selected from the group comprising bis (di-t-butyl phosphino)-o-xylene; 1,2 bis (diadamantylphosphinomethyl) benzene; 1,2 bis (diadamantylphosphinomethyl) naphthalene; 1,2 bis (di-t-pentyl phosphino)-o-xylene; and bis 1,2 (di-t-butyl phosphino) naphthalene.

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28. The process as claimed in any preceding claim, wherein the mol:mol range of compounds of formula (I) to Group VIII metal is in the range of 1:1 to 3:1.

20 29. The process as claimed in claim 28, wherein said mol:mol range is in the range of 1:1 to 1.25:1.

25 30. The process as claimed in any preceding claim, wherein the Group VIII metal is selected from the group comprising: cobalt, nickel, palladium, rhodium, ruthenium and platinum.

31. The process as claimed in claim 30, wherein said Group VIII metal is rhodium.

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32. The process as claimed in any preceding claim, wherein said chlorine moiety is present in at least said Group VIII metal compound and said compound is

- selected from the group comprising: $[\text{RhCl}(\text{CO})_2]_2$,
 $[\text{RhCl}(\text{Cod})_2]_2$, $\text{RhCl}_3 \cdot x\text{H}_2\text{O}$, $[\text{RhCl}(\text{Norbornadiene})]_2$,
 $[\text{RhCl}(\text{Cyclooctene})_2]_2$, Chloro(1,5-hexadiene)-
rhodium(I)dimer, Mu-dichlorotetraethylene-dirhodium,
5 (bicyclo[2,2,1]hepta-2-5-diene)chlororhodium(I)dimer.
33. The process as claimed in any preceding claim,
wherein said chlorine moiety is present in at least
said Group VIII metal compound and said compound is
10 selected from the group comprising: $[\text{RhCl}(\text{CO})_2]_2$,
 $[\text{RhCl}(\text{Cod})_2]_2$ and $\text{RhCl}_3 \cdot x\text{H}_2\text{O}$.
34. The process as claimed in any one of claims 2 to 33,
wherein said chlorine moiety is present in at least
15 said solvent and said solvent is selected from the
group comprising dichloromethane, chlorobenzene, o-
dichlorobenzene, m-chlorobenzene, carbon
tetrachloride, trichloroethanes, dichloroethanes,
chlorofluorocarbons (CFC's), tetrachloroethanes and
20 tetrachloroethene.
35. The process as claimed in claim 34, wherein said
solvent is dichloromethane.
- 25 36. The process as claimed in any preceding claim,
wherein said ethylenically unsaturated compound has 2
to 20 carbon atoms.
37. The process as claimed in claim 36, wherein said
30 compound has 5 to 15 carbon atoms.
38. The process as claimed in claim 36, wherein said
compound has 6 to 12 carbon atoms.

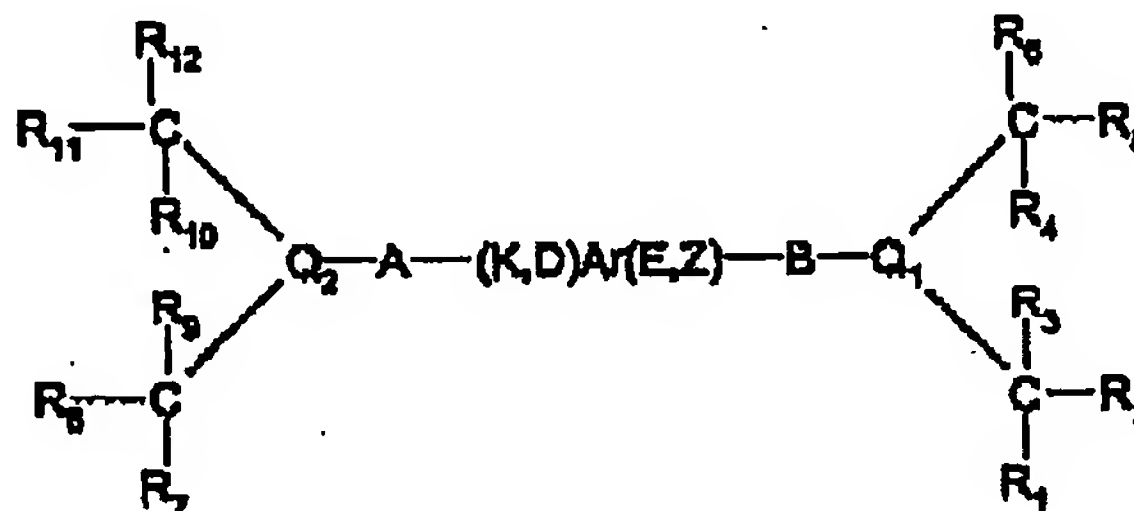
39. The process as claimed in any preceding claim, wherein said ethylenically unsaturated compound is selected from the group comprising ethene, propene, 1-butene, 2-butene, isobutene, 1-pentene, 2-pentene, 3-pentene and branched isomers thereof, 1-hexene and its isomers, 1-heptene and its isomers, 1-octene and its isomers, 1-nonene and its isomers, 1-decene and its isomers, the C₁₁-C₂₀ alkenes and their known isomers, 3-pentenitrile, methyl-3-penteneoate, 1,3 butadiene, 1,3-pentadiene, 1,3 hexadiene, 1,3 cyclohexadiene, 2,4-leptadiene, and 2-methyl 1,3 butadiene.
40. The process as claimed in any preceding claim, wherein the solvent is formed by one or more of the reactants, products or by-products of the process rather than being a separate entity.
41. A process for the hydroformylation of ethylenically unsaturated compounds as described hereinbefore with reference to the examples herein.

ABSTRACT

Process for the Hydroformylation of Ethylenically
Unsaturated Compounds

5 The present invention provides a process for the hydroformylation of ethylenically unsaturated compounds, which process comprises reacting said ethylenically
 10 unsaturated compound with carbon monoxide and hydrogen, in the presence of a catalyst system and a solvent, the catalyst system obtainable by combining:

- a) a metal of Group VIII or a compound thereof; and
 15 b) a bidentate phosphine of general formula (I)



wherein:

Ar is a bridging group comprising an optionally
 20 substituted aryl moiety to which the phosphorus atoms are linked on available adjacent carbon atoms;

A and B each independently represent lower alkylene;

25 K, D, E and Z are substituents of the aryl moiety (Ar); or two adjacent groups selected from K, Z, D and E together

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with the carbon atoms of the aryl ring to which they are attached form a further phenyl ring, which is optionally substituted by one or more substituents;

5 R¹ to R¹⁸ each independently represent lower alkyl, aryl, or Het;

R¹⁹ to R²⁷ each independently represent hydrogen, lower alkyl, aryl or Het;

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Q¹, Q² and Q³ (when present) each independently represent phosphorous, arsenic or antimony and in the latter two cases references to phosphine or phosphorous above are amended accordingly,

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the process characterised in that a chlorine moiety is present in at least one of the said Group VIII metal compound or said solvent.

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